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C 1s Autoionization Study of Electron Hopping Rates in Solid C_{60}

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We present C 1s autoionization studies of condensed and Xe matrix-isolated C_{60} molecules which give direct information on electron hopping rates in solid C_{60} in the presence of a C 1s vacancy. These rates vary dramatically for the first three C 1s absorption excitation maxima in a pattern consistent with strong electron-electron correlations. Hopping associated with the second excited state involves extramolecular screening comparable to the Mott-Hubbard pseudogap predicted for K_3C_{60}, suggesting intramolecular correlations do not dominate electron transport in the alkali fullerides.

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In the short time since the discovery of a method [1] to synthesize macroscopic quantities of C_{60} (buckminsterfullerene [2]), much has been learned about the structure of fullerite [3]. At room temperature, the solid takes the form of a face-centered-cubic lattice, in which the molecules are rotationally disordered and spinning rapidly [4,5]. Cooling brings about a phase transition to a simple-cubic structure in which the molecular rotations are hindered, but the orientations remain disordered. Models of this phase transition which assume van der Waals bonding and repulsive nearest-neighbor Coulomb interactions have correctly predicted the low temperature structure [6]. Thus the structural properties of solid C_{60} are consistent with those of a van der Waals, or molecular, solid.

The discovery of superconductivity in alkali fullerides such as K_3C_{60} [7] has spurred intense interest in those materials. It has been found that they can be considered in zeroth approximation as face-centered-cubic lattices of $(C_{60})^{3-}$ molecules with weak intermolecular bonding [8,9], and the superconductivity mechanism appears to be driven by a unique combination of molecular and solid state properties [8]. A possible drawback of the theoretical work thus far is the omission of electron-electron correlations, which were recently elucidated [10]. The correlation energy ($U \sim \frac{3}{2}$ eV) for two excess charges on one C_{60} molecule in the solid has been shown to be large compared to a typical theoretical bonding interaction ($W \sim \frac{1}{2}$ eV) [9] for levels near the Fermi energy [10]. This suggests that all stoichiometric alkali fullerides are Mott-Hubbard insulators [11] with a minimum electronic transport gap (or "pseudogap") of the order of 0.7 eV [10]. In this picture, material defects are required to explain the measured conductivity and superconductivity.

On the other hand, recent calculations indicate that intermolecular Coulomb screening, V, acts to reduce U, i.e., $(U-V)/W \sim 1$ [12]. In this model, the additional potential energy U required for one electron to hop to the same C_{60} molecule as another is compensated signficantly by the potential energy (V) of their interaction before the transition, thus making the total cost in correlation energy for such a microscopic conduction process comparable to the bonding interaction. This result, if confirmed, implies that *stoichiometric* alkali fullerides with partially filled bands can be conductors in spite of correlations. This conclusion is dependent in large measure, however, on the magnitude of W, which is difficult to determine experimentally [13] and suffers on the theoretical side from uncertainty due to possible vibronic effects [14], which tend to reduce W [11]. So far, no band calculation for solid C_{60} or its compounds has included the effects of vibronic coupling, leaving open the question of whether indeed $(U-V)/W \sim 1$, and thus there remains a strong question from the theoretical side of whether electron hopping may occur for a stoichiometric alkali fulleride.

In this Letter we present experimental determinations of electron hopping out of three conduction orbitals of solid C_{60} which are independent of the theoretical uncertainties discussed above. We use a new method based on autoionization spectroscopy near the C 1s threshold. In essence, we pump a C 1s electron to a bound state, whose intermolecular bonding interactions we then probe by comparing the transition rates out of this excited state when the probed molecules are in two environments: (1) the solid and (2) matrix isolated in Xe, which as we explain below should be an excellent approximation to a gas phase measurement. The Coulomb attraction between the core hole and pumped electron plays the role of U. We then use the decay of the core hole as a clock to measure the hopping rate for the excited electron away from the probed molecule. Since this channel is forbidden in the Xe matrix, intensity changes for a given transition energy between the two environments give a direct measure of electron hopping rates. This approach has the advantage that preparing stoichiometric, pure C_{60} films is straightforward, sidestepping many of the difficulties which have been found for alkali fulleride films [13]. For an electron pumped to the C 1s threshold, correlation effects appear to totally localize the excited state to the probed molecule. However, for the next transition 1.3 eV higher, intermolecular screening of the order of the pseudogap of 0.7 eV brings about a hopping rate roughly

equal to the core decay rate of $\sim 1.7\times10^{14}$ Hz. *This is experimental proof that intermolecular screening can overcome the Coulomb barrier to electron transport in the alkali fullerides*, and suggests that Mott-Hubbard correlations do not dominate the physics of electron transport in the fulleride superconductors.

The spectra were taken at beam line 22 [15] at MAX Lab, which has a sample preparation chamber and analysis chamber (base pressures 1.0×10^{-10} and $\sim 5\times10^{-11}$ Torr, respectively) with a yield detector for soft-x-ray absorption determination and a high-efficiency electron energy analyzer. Commercially produced C_{60} which we checked by mass spectrometry was evaporated from a radiatively heated Ta crucible onto a clean Au(110) substrate at pressures of 3×10^{-10} Torr or less. In the matrix-isolation experiments the substrate was cooled to 30 ± 10 K and the preparation chamber was held at 3.5×10^{-7} Torr of Xe during C_{60} evaporation at a rate of ~ 0.14 saturated layer/min. Xe was chosen for its high melting point, lack of interfering core lines, and large band gap [16], which encompasses most of the π-like manifold [17] including the highest occupied molecular orbital (HOMO) and next two occupied bands, lowest unoccupied molecular orbital (LUMO), and all of the bound states at higher energy. C 1*s* absorption spectra were acquired in the total yield mode and normalized by yield from atomically clean metal surfaces [Au(110) and Mo(110)]. Energy resolution was ~ 0.16 eV for photons, 0.30 eV for electrons. To obtain the intensities of the participator autoionization peaks discussed below, we subtracted photoemission backgrounds taken at 280 eV photon energy, as well as a first order C 1*s* photoemission spectrum fit to the second order line.

We first discuss the C 1*s* absorption spectra for the two cases (see Fig. 1). Intermolecular bonding effects are apparent in solid C_{60} in the generally greater broadening found for the thick film spectrum compared to the matrix isolated. In particular, the second and third structures in the spectrum of the solid are noticeably broader than in that of the molecule. This greater broadening is independent of the temperature of the thick film for $30 < T < 300$ K, and is well modeled by convolution of the matrix-isolated C_{60} spectrum with a 0.25-eV-wide Gaussian. The structures labeled (a)–(c) can be identified with core-hole-perturbed levels derived [18] from the $5t_{1u}$ (LUMO), $2t_{1g}/5t_{2u}$, and $8h_g$ orbitals of C_{60}, respectively, although these details are not crucial in what follows. It is difficult to obtain quantitative information about bonding properties from the absorption spectra alone, however, for several reasons: The hybridization-induced broadening can vary with orbital, coupling to vibrational excitations probably changes between the two environments, and structures (b) and (c) overlap significantly. We therefore focus on the participator autoionization intensity at the energies of the peaks (a)–(c).

We have discussed autoionization of solid C_{60} previously [19]. Raw spectra for solid and matrix-isolated C_{60} at

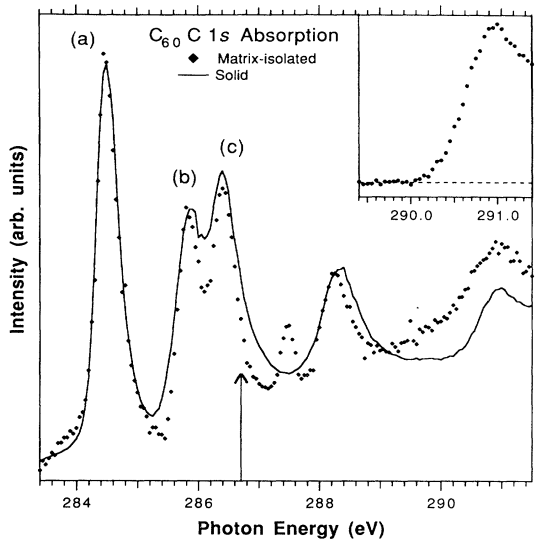

FIG. 1. C 1*s* absorption spectra of solid and Xe matrix-isolated C_{60}. The inset is a closeup of the data for solid C_{60} in the range of the ionization threshold, and the arrow indicates the lower limit for the electron affinity of solid C_{60} when referenced to that threshold. Points (a)–(c) are the excitation energies used for autoionization discussed in the text. We attribute the small peak at 287.4 eV to slight CO contamination [24], which will not affect the analysis of the transitions at lower energies.

$h\nu = 284.50\pm0.05$ eV are shown in Fig. 2, normalized to yield the relative intensity per molecule by dividing by the intensity of the C 1*s* line excited by second order light (indicated in the figure) [20]. The so-called participator autoionization [21] channel, which yields a final state equivalent to that of photoemission, appears at the same binding energy. The fundamental gap of C_{60} (~ 1.6 eV) causes the kinetic energy of electrons emitted in other, e.g., spectator transitions to be reduced relative to the HOMO participator transition, yielding spectral structure at least 1.6 eV to lower kinetic energy. Empirically [19], the strength of the participator autoionization dominates that of direct photoemission. *Thus a HOMO participator peak is unambiguous evidence of localization of the excited core electron to the probed molecule.*

In Fig. 3 we compare the first two autoionization structures at excitation energies (a)–(c) for the two environments. Although not required in our main conclusion, we indicate the implicit hopping interaction of the excited state in each case. The number derived for this interaction can be understood in a manner similar to charge transfer screening of a core-excited physisorbate [22], in which we postulate that the weak-coupling hopping rate can be characterized by exponential decay of the excited state via transfer of the promoted electron to a nearest neighbor. The intensity changes shown in Fig. 3 represent the result of competition between this rate and that of core hole annihilation, plus a small contribution due to the additional broadening of the structures in the solid

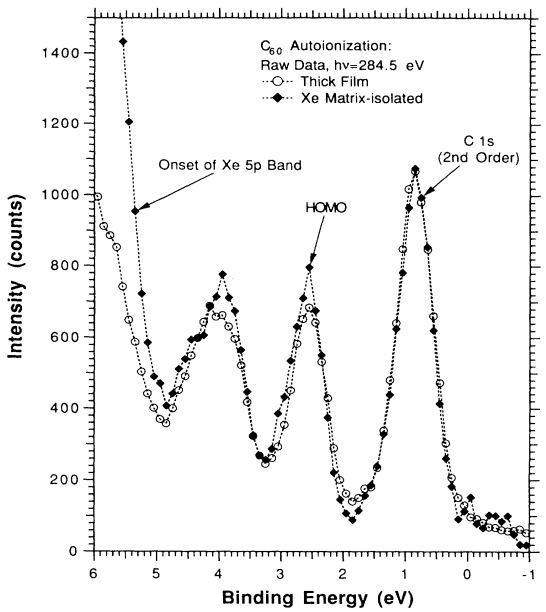

FIG. 2. Autoionization spectra after C $1s \rightarrow$ LUMO excitation [(a) in Fig. 1] for solid and Xe matrix-isolated C_{60}. The matrix-isolated spectrum has had a constant background of 970 counts subtracted.

absorption spectrum, which reduces the excitation probability, and thus the deexcitation intensity by about 10%. C $1s$ lifetimes are found to vary with atomic environment [23] and with the presence [24] or absence [25] of an excited core electron. Because the hopping determined here implies a certain delocalization of the electron, the value of lifetime energy broadening falls within these two limits [24,25], i.e., $\Gamma = 110 \pm 40$ meV, equivalent to a lifetime of $6 + 2.5$ fs.

Determination of the hopping rate is then straightforward: First, we note that the participator autoionization events represent only a small fraction of the total Auger-like decay of the excited state, as can be seen from data over a wider electron energy range [19]. Thus the C $1s$ lifetime, which is limited by the total Auger and autoionization transition rate, will not change appreciably even on complete loss of the participator channel. Assuming exponential rates for both core hole decay and electron hopping, it is simple to show that $\Delta/\Gamma = dI/I_{\text{solid}}$, where Δ is the hopping bandwidth, dI the change in intensity of the participator line, I_{solid} the intensity for solid C_{60}. Thus an electron is well localized to the core-excited molecule if placed in the LUMO, has a relatively large hopping rate ($\sim 1.7 \times 10^{14}$ Hz) in the next level studied here, and is more localized again at the third. A negligible hopping bandwidth for the LUMO is within our experimental uncertainties. These results are qualitatively consistent with the overall trend of the broadening in the peaks associated with (a)–(c). We wish to emphasize again, however, that our primary goal is simply to show experimentally the existence of intermolecular hopping in the presence of the core hole.

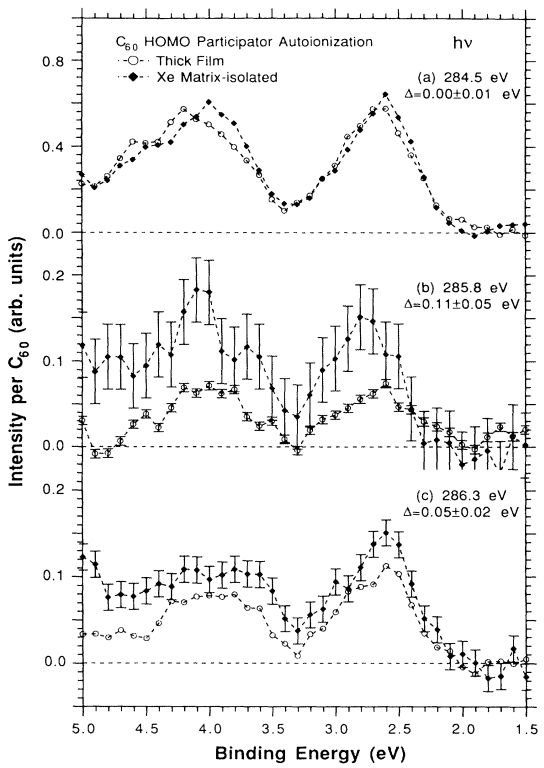

FIG. 3. Spectra in the vicinity of the HOMO participator for solid and Xe matrix-isolated C_{60}, after excitation to final states indicated by (a)–(c) in Fig. 1.

To relate these results to the problem of correlation and hopping in stoichiometric A_3C_{60}, we first determine the core-valence correlation energy. Since U corresponds both to two-electron repulsion and to electron-hole attraction, which have similar values both experimentally and theoretically [10,12], different methods can be used to determine it. One is to consider the process in which an electron is excited from the HOMO to the LUMO. Then the energy required to remove this electron to infinity compared to the electron affinity of neutral C_{60} is U. For the free molecule this has been measured to be ~ 3 eV if one considers Fig. 4 of Ref. [26] and recalls the ionization potential of neutral C_{60} of 7.6 eV [14]; quite similar values are found in other approaches [10,12]. Polarization of the neighboring molecules reduces U by ~ 1.5 eV [10,12]. Put in another way, the energy released by bringing an electron from infinity and depositing it in the t_{1u} orbital in the presence of a valence hole is U greater than that released for the neutral molecule. One can similarly determine the core-valence correlation energy, which we denote U_c. We take the electron affinity of solid C_{60} to be $E_V - 3.3$ eV, where E_V is the vacuum level; this value is based on the electron affinity of 2.6 eV measured by photodetachment of $(C_{60})^-$ [26] and polarization screening of 0.7 eV [10,27]. We now require the C $1s$ ionization potential of solid C_{60}. We have made a direct determination by comparing the continuum onset for solid C_{60}, shown in the inset of Fig. 1, to that of a

weakly bound monolayer adsorbed on Al(111), for which the ionization potential has been determined [27]. This yields a solid C_{60} C 1s ionization potential of 290.0 ± 0.1 eV. The t_{1u} level for core-excited C_{60} [(a) in Fig. 1] is located at 284.5 eV $= E_V - 5.5 \pm 0.2$ eV; hence $U_c = 5.5 \pm 0.2$ eV $- 3.3 \pm 0.2$ eV $= 2.2 \pm 0.3$ eV. The one-electron energy of a nearest neighbor t_{1u} level is indicated in Fig. 1 by the arrow. Thus, we have shown that for electronically independent molecules there is a minimum barrier for hopping from the molecule we probe in this experiment of 2.2 ± 0.3 eV, 0.9 ± 0.3 eV, and 0.3 ± 0.3 eV for transitions (a)–(c), respectively.

It is clear from these numbers that hopping from the core-perturbed t_{1u} molecular subbands should be negligible due to the large barrier just derived, since the theoretically predicted bandwidth of this level in the ground state [9,17] is only about $\frac{1}{2}$ eV. This agrees with our results. The small size of the core hole perturbation on the one-electron energies, as shown, e.g., by calculations of the electronic structure of the $Z+1$ molecule $C_{59}N$ [28] to be of the order of 0.3 eV [29], suggests that U_c is responsible for the localization of the excited state to the probed molecule. This also explains the similarity in width of the t_{1u}-derived peak for the solid and matrix-isolated C 1s absorption spectra.

It is the case of hopping from the second core-excited state (b) that makes clear the distinction between single-particle and many-body effects in this problem. The arrow in Fig. 1 indicates the one-electron energy at which one could locate the t_{1u} band of solid C_{60} based on the electron affinity as discussed above. The barrier for hopping to this orbital in the picture used by Lof *et al.* of electronically independent nearest neighbor molecules is of the order of 0.9 eV. The hopping we measure requires that the energy of the system be lowered significantly from that given in such a picture by additional screening; the simplest explanation is that this is an effect of the transferred electron. This screening, of the order of 1.4 eV in the case of an isolated pair of molecules 10 Å apart, is, however, reduced by the polarization of the surrounding lattice in the manner described by Antropov, Gunnarsson, and Jepsen [12], for a lower net effect. Thus we find the net screening to be of the order of the 0.7 eV pseudogap predicted for stoichiometric K_3C_{60} [10], or larger. *Hence extramolecular screening such as that calculated by Antropov, Gunnarsson, and Jepsen [12] can indeed explain why single-crystal samples of K_3C_{60} [30] are not Mott-Hubbard insulators.* Our results nevertheless strongly support the contention of Lof *et al.* [10] that electron-electron correlations are important in understanding the electronic transport properties in these materials, suggesting that correlations will therefore likely need to be included in models of alkali fulleride superconductivity [8].

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